# A Micro-titrimetric Method for the Determination of the Oxirane Functional Group

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A micro-titrimetric method for the determination of the oxirane functional group by using quaternary ammonium halide and perchloric acid has been developed. The method can be used for the determination of compounds with about 2 μequivalents of oxirane content.

Fatty acids containing the oxirane functional group occur widely in seed oils and are usually present as long-chain glycerides. Various methods have been described for determining the oxirane content of these epoxy compounds. The most notable of these are the hydrohalogenation methods carried out in non-aqueous solvents for macro determination of the epoxy group. In 1956, Durbetaki[1] reported a method involving the use of hydrogen bromide in glacial acetic acid as the hydrohalogenating agent, and in 1964 this procedure became the A.O.C.S. Tentative Method, Cd 9–63 "Oxirane Oxygen."[2,3] Recently Jay[4] described a method, which he applied to the determination of epoxy resins and aziridines. The method differs from the Durbetaki method in that it involves *in situ* generation of hydrohalic acid by the reaction of standard perchloric acid with tetra-alkylammonium halide. The acid thus liberated immediately reacts with the oxirane linkage.

The present paper describes a method, which is essentially an extension of Jay's modified hydrobromination procedure, for the determination of epoxy groups in compounds available in micro amounts.

## Experimental

### Apparatus—

The apparatus consisted of an all-glass microburette with automatic zero adjustment, 50 and 100-ml glass-stoppered conical flasks, micropipettes and other suitable pipettes, and glass-coated magnetic elements. All glassware used was cleaned and dried before use.

### Reagents—

*Chloroform, E. Merck.*

*Glacial acetic acid, analytical-reagent grade.*

*Standard* 0·002 N *perchloric acid in glacial acetic acid*—This was prepared by dilution of a 0·1 N perchloric acid solution with glacial acetic acid in a graduated flask. A 0·1 N perchloric acid solution in glacial acetic acid was initially standardised against analytical-reagent grade sodium carbonate as follows. About 0·1 g of sodium carbonate (previously dried at 105° ± 5° C to constant weight) was accurately weighed into a 100-ml stoppered Erlenmeyer flask and 5 ml of glacial acetic acid were added to dissolve it, followed by 4 ml of chloroform. The test solution was stirred magnetically and titrated with perchloric acid solution under moisture-free conditions until a blue - green end-point was reached, by using 4 drops of indicator solution. From the titre reading and weight of sodium carbonate, the exact concentration of 0·1 N perchloric acid solution was found.

*Tetra-ethylammonium bromide solution, 5 per cent. in glacial acetic acid.*

*Crystal violet solution, 0·1 per cent. in glacial acetic acid.*

*Solution of test sample, 0·1 to 0·5 per cent. in benzene or xylene.*

The concentration of the dilute perchloric acid reagent was also determined by the micro-titrimetric procedure described below.

### Procedure for micro analysis—

A suitable volume of the test sample solution was added from a pipette into a 50-ml Erlenmeyer flask fitted with a glass stopper, then 4 ml of glacial acetic acid, or preferably 4 ml

of chloroform, were added to the solution. This was followed by accurate addition of 2 ml of tetra-ethylammonium bromide reagent from a pipette, then 0·05 to 0·1 ml of indicator solution was finally added to the test solution. The solution was then stirred magnetically at a slow rate to avoid splashing, and titrated with standard 0·002 N perchloric acid reagent until the colour of the solution changed from blue - green to just green. A blank was carried out under identical conditions. The volume of benzene or xylene (added as test solution) was kept constant but at a minimum in all determinations. The perchloric acid reagent was added from an all-glass automatic microburette under moisture-free conditions.

TABLE I

DETERMINATION OF OXIRANE FUNCTIONAL GROUP IN EPICHLOROHYDRIN BY THE PRESENT METHOD

| Epichlorohydrin | Amount analysed, μequivalents of oxirane content | Oxirane-oxygen found, per cent. | Epichlorohydrin found, per cent. | Oxirane-oxygen content: Mean deviation | Oxirane-oxygen content: Standard deviation |
|---|---|---|---|---|---|
| Oxirane-oxygen 16·61 per cent. | 5 | 16·65<br>16·65<br>16·74<br>16·56<br>16·56<br>Mean 16·63 | 96·23<br>96·23<br>96·81<br>95·50<br>95·50<br>Mean 96·05 | 0·06 (0·06) | 0·08 (0·08) |
| Epichlorohydrin 95·98 per cent. (determined by macro method) | 2·5 | 16·84<br>16·65<br>17·03<br>16·84<br>17·22<br>Mean 16·91 | 97·27<br>96·23<br>98·45<br>97·27<br>99·54<br>Mean 97·75 | 0·17 (0·30) | 0·22 (0·78) |
| | 1 | 17·03<br>17·03<br>17·50<br>17·98<br>17·50<br>Mean 17·41 | 98·45<br>98·45<br>101·20<br>104·00<br>101·20<br>Mean 100·66 | 0·30 (0·80) | 0·40 (0·98) |

Values in parentheses were calculated on the basis of oxirane content obtained by the macro method.

TABLE II

DETERMINATION OF OXIRANE FUNCTIONAL GROUP IN *Vernonia anthelmintica* SEED FAT BY THE PRESENT METHOD

| *Vernonia anthelmintica* seed fat | Amount analysed, μ equivalents of oxirane content | Oxirane-oxygen found, per cent. | Epoxy-oleic acid found, per cent. | Oxirane-oxygen content: Mean deviation | Oxirane-oxygen content: Standard deviation |
|---|---|---|---|---|---|
| | 5 | 3·80<br>3·80<br>3·76<br>3·68<br>3·84<br>Mean 3·78 | 70·31<br>70·31<br>69·56<br>68·08<br>71·11<br>Mean 69·87 | 0·03 (0·04) | 0·04 (0·07) |
| Oxirane-oxygen 3·80 per cent. Epoxy-oleic acid 70·31 per cent. (determined by macro method) | 2·5 | 3·59<br>3·93<br>3·59<br>3·68<br>3·76<br>Mean 3·71 | 66·42<br>72·71<br>66·42<br>68·08<br>69·56<br>Mean 68·64 | 0·11 (0·14) | 0·14 (0·17) |
| | 1 | 4·17<br>4·03<br>4·03<br>3·88<br>3·89<br>Mean 4·00 | 78·94<br>74·96<br>74·96<br>71·78<br>71·96<br>Mean 74·48 | 0·11 (0·20) | 0·12 (0·25) |

Values in parentheses were calculated on the basis of oxirane content obtained by the macro method.

Samples analysed were epichlorohydrin (B.D.H., purity 96·0 per cent. based on oxirane-oxygen analysis) and *Vernonia anthelmintica* seed fat. The seed fat was obtained by extraction with light petroleum (60° to 66° C) of the crushed seeds, drying the extract over anhydrous sodium sulphate and subsequent filtration of the extract, followed by removal of the solvent from the filtrate by distillation under reduced pressure. Oxirane contents in these samples were checked by the macro-hydrobromination method as reported by Jay. Some typical results are recorded in Tables I and II.

## Discussion

The hydrobromination method as modified by Jay has been preferred to the Durbetaki method as the titrant possesses better storability, the method permits reasonably rapid addition of perchloric acid and the end-point is sharper. Adaptation of the method to deal with micro amounts yielded results that were in good agreement with the values obtained by the macro method. Consistent and reliable results are obtained for samples with as low as 2 $\mu$equivalents of oxirane content (Tables I and II). Use of high boiling solvents such as benzene and xylene, which are inert under the reaction conditions, for dissolution of test samples ensures better results. However, the volume of benzene or xylene used has to be kept at a minimum in proportion to the volume of acetic acid used to avoid precipitation of the quaternary ammonium halides, which are of limited solubility in the former solvents. The addition of aprotic solvents, such as chloroform, gives sharper end-points. This is possibly because such solvents tend to depress solvolysis of the neutralisation products. The concentration of the quaternary ammonium halide in acetic acid is not critical but the halide used should be in sufficient excess of the amount required by the stoicheiometry of the reaction. It is also important to add the same volume of crystal violet solution (which should not exceed 0·1 ml for a 0·1 per cent. solution) in a set of determinations to obtain uniform results. Application of the method to the determination of the oxirane functional group in *Vernonia anthelmintica* seed fat isolated by preparative thin-layer chromatography showed satisfactory results. The method combined with chromatographic techniques may prove useful for determination of a wide variety of epoxy compounds as such or samples obtained during various stages of processing.

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